



THEORY OF DESORPTION OF SURFACE BOUND POSITRONS

R.Y. Levine and L.M. Sander

Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA

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A theory is given for the conversion of positrons bound at metal surfaces to free positronium via electron pickup. The method is applied to Al and Ni.

Desorption of positrons from surface bound states on a metal has been observed in a number of experiments.¹ The results are interpreted by supposing that a positron is in a surface state from which it is energetically favorable to pull an electron over the work function barrier in the metal and form a positronium bound state. In practice these processes are identified when the ground surface state of the positron is stable but an excited state is unstable; then the desorption shows a characteristic temperature dependence. In this paper we give a microscopic theoretical description of the desorption process.

Our essential problem is that the important states of the electrons are quite different inside and outside the metal. Inside, there are many electrons (which we suppose, for simplicity, not to interact) in a Fermi sea which screen out the Coulomb field of the positron in a short distance. Outside, an electron can be highly correlated with the positron in a bound state (positronium). These states arise, of course, from the same microscopic Hamiltonian, but in a complex way. To make a tractable theory we follow methods used in the theory of quantum tunneling² and expand the exact wave function in the basis states of two approximate Hamiltonians.

We suppose that the metal surface is at $x=0$ and has characteristic width a . In the initial state all the electrons are inside and the approximate Hamiltonian is

$$H_i = \sum_{j=1}^N \left(-\frac{\hbar^2 \nabla_j^2}{2m_e} + W\theta(x_j) \right) - \frac{\hbar^2 \nabla_p^2}{2m_p} + V(\vec{r}_p) \quad (1a)$$

$$\sum_{j=2}^N \left(-\frac{\hbar^2 \nabla_j^2}{2m_e} + W\theta(x_j) \right) - \frac{\hbar^2 \nabla_p^2}{2m_p} + V(r_p) - \frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{e^2}{|\vec{r}_1 - \vec{r}_p|} + W\theta(x_1) \quad (3)$$

Here e, p refer to electron and positron and W

($= \phi_- + e_F$) is the potential binding the electrons. Also, ϕ_- is the work function and e_F the Fermi energy; $V(\vec{r}_p)$ is the positron image potential.

For the final state we "turn on" the electron-positron interaction:

$$H_f = \sum_{j=2}^N \left(-\frac{\hbar^2 \nabla_j^2}{2m_e} + W\theta(x_j) \right) - \frac{\hbar^2 \nabla_p^2}{2m_p} - \frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{e^2}{|\vec{r}_1 - \vec{r}_p|} \quad (1b)$$

Here \vec{r}_1 is the coordinate of the pickup electron. The physical justification for this is the change in the screening of the electron-positron interaction mentioned above. H_i and H_f are the two approximate Hamiltonians.

The initial state is given by $\phi_0 = \psi_\chi$, where ψ is the filled Fermi sea and $\chi(\vec{r}_p)$ is the bound positron surface state. We take the time-dependent state of the system to be (following Bardeen²):

$$e^{-iE_0 t/\hbar} \phi_0 + \sum_{\nu} a_{\nu}(t) e^{-iE_{\nu} t/\hbar} \phi_{\nu}(\vec{r}_e, \vec{r}_p) \quad (2)$$

where $\phi_{\nu} = \psi_{\vec{k}} \psi_{\vec{k}'}; \psi_{\vec{k}}$ is a state of the metal with a hole in \vec{k} and $\psi_{\vec{k}'}$ is the positronium bound state with center of mass momentum \vec{k} in the positive direction (away from the metal). Substitution of this wavefunction into the time dependent Schrodinger equation with the exact Hamiltonian,

gives an equation for a_{ν} :

$$i\hbar \dot{a}_{\nu}(t) e^{-iE_{\nu} t/\hbar} = -e^2 \langle \psi_{\nu} | \frac{1}{|\vec{r}_e - \vec{r}_p|} | \phi_0 \rangle e^{-iE_0 t/\hbar} + 0(a_{\nu}) \quad (4)$$

Solving the equation above to lowest order in $a_v(t)$ and assuming $a_v(-\infty)=0$ gives

$$a_v(t) = \frac{ie^2}{\hbar} \frac{e^{i(E_v - E_0)t/\hbar}}{(E_v - E_0 + i\eta)} \langle \psi_v | \frac{1}{|r_e - r_p|} | \phi_0 \rangle, \quad (5)$$

where $\eta \rightarrow 0$.

We assume the surface positron is thermalized so one can assume it has small momentum along the surface. Letting x be the direction perpendicular to the metal surface, we have $\phi_p(\vec{r}_p) = \phi_p(x_p)/\sqrt{A}$ (A =surface area). For thermal desorption ϕ_p is the first excited state. We anticipate that the only important quantities in ϕ_p are the decay lengths into the metal and the vacuum. These we take from ground state wave functions calculated by Nieminen and Hodges³. Thus we approximate:

$$\phi_p(x) = \begin{cases} Ae^{\gamma x} & x < a \\ B(x+x_0)e^{-\beta x} & x > a \end{cases}, \quad (6)$$

where A, B, x_0, γ, β are determined by matching conditions and a variational calculation. The electron state is given by

$$(\phi_{k_x}(x) e^{iky + ik_z z})/\sqrt{A}, \quad (7a)$$

where

$$\phi_{k_x}(x) = \begin{cases} C(e^{ik_x x} + re^{-ik_x x}) & x < 0 \\ De^{-\kappa x} & x > 0 \end{cases}. \quad (7b)$$

Here C, D , are determined by normalization and matching conditions at the surface barrier, and r is the reflection coefficient. There is, of course, more complication for nontrivial band structures. We will assume that this is accounted for by taking m_e to be an effective mass in

$$\kappa = \sqrt{\frac{2m_e \Delta E}{\hbar^2}} \quad (8a)$$

where

$$\Delta E = (\phi_- + \epsilon_F - \frac{\hbar^2 k^2}{2m_e}). \quad (8b)$$

This value of κ is substituted in Eq. (7b). The final positronium state is given by

$$\phi_{\vec{k}}(\vec{r}_1, \vec{r}_p) = \frac{\exp(-|\vec{r}_1 - \vec{r}_p|/2a_0) e^{i\vec{k} \cdot (\vec{r}_1 + \vec{r}_p)}}{\sqrt{8\pi V a_0^3}} \quad (9)$$

where V is the total volume and a_0 is the Bohr radius.

We have the constraints of momentum conservation along the surface and energy conservation:

$$k_y = K_y, \quad k_z = K_z, \quad (10a)$$

$$\text{and} \quad E_v = E_0, \quad (10b)$$

$$\text{where} \quad E_v = E_{N-1} + \frac{\hbar^2 K^2}{4m} - \frac{\hbar^2 k^2}{2m_e} - E_s, \quad (10c)$$

$$\text{and} \quad E_0 = (E_N - E_p). \quad (10d)$$

In Eqs. (10) we take E_s to be the positronium binding energy (-0.5 Ryd.); E_p the positron surface binding energy and E_N, E_{N-1} are the energies of N and $N-1$ electrons in the metal. The work function ϕ_- is $(E_N - E_{N-1})$. The rate of desorption is given by applying Fermi's Golden Rule to Eq. 2:

$$R = \frac{2\pi}{\hbar} \frac{e^4}{(8\pi V a_0^3)} \sum'_{\vec{k}} \sum_{\vec{K}} \delta_{k_y, K_y} \delta_{k_z, K_z} \delta(E_v - E_0) |J(\vec{k}, \vec{K})|^2 \quad (11)$$

Where \sum' is the sum over center of mass positronium momentum and J is the overlap integral in Eq. (2). Note that for k_x satisfying the constraints, $-k_x$ contributes as well.

The parameter a in Eq. (6) represents the width of the metal surface. We assume the electrons significantly overlap the positron outside of the positron image charge plane; this occurs on the vacuum side of the first layer of ions where electron wavefunctions are exponentially decaying. We chose a to be the approximate image potential width as calculated by Nieminen and Manninen⁴. This gives $a = 1.7A$. We found our results to have a weak dependence on this parameter over a range 1-3A.

Rosenberg, Weiss, and Canter⁵ have measured the activation energy for Al(100) to be .44 eV. Nieminen and Hodges³ give a ground state energy of 2.1 eV which yields $E_p = 1.66$ eV. We take their ground state decay lengths to be .29A and .28A for β and γ respectively. Other standard values for Al ($\phi_- = 4.41$ eV, $\epsilon_F = 11.7$ eV) give a range for the positronium energy of $0 < E_k < .73$ eV at low temperatures. The calculated rate ranges from $(1.8-2.6) \times 10^{14} (\text{sec})^{-1} (\text{eV})^{-1} (\text{strad})^{-1}$. Note that this rate is small enough so that thermal equilibrium between ground and first excited positron surface states can probably be established. Figure 1 exhibits the angular dependence of the rate at various energies ($E = .1, .3, .5, .7$ eV). The most energetic positronium have a 70-80% drop in the rate at large angles. The broad angular distribution of the positronium arises from the large electron momentum along the surface. This is an interesting feature which could be measured. In figure 2, the dependence of the rate in the forward direction ($\theta = 0$) on positronium energy is shown. We found at low energy the rate depends only on the allowed phase space.

These results are most directly comparable to those of Mills and Pfeiffer⁶ who have measured the velocity distribution of thermal positronium emission from Cu(111) in the forward direction at $T \approx 1000^\circ\text{K}$. They fit their data with a Boltzmann factor of the positronium kinetic energy times a quadratic function of the positronium velocity. We can reproduce the qualitative features of their result by multiplying the rate shown in Fig. 2 by the Fermi distribution of the pickup electrons. We obtain the Boltzmann factor (the tail of the Fermi distribution) for the most energetic

We have also applied our technique to ferromagnetic Ni following a suggestion by J. Rose.⁸ This is particularly interesting because a polarized positron beam could be used to measure the polarization of the pickup electron.⁹ Unfortunately, the complicated band structure of Ni makes it difficult for us to give more than a rough estimate and the thermally desorbed positron component is rather small⁵ below the Curie temperature of Ni.

We make some drastic approximations; we neglect s-d hybridization completely and assume free electron s and d bands with effective masses $m_s = m_e$ and $m_d > m_e$. We consider electron pickup at the Fermi surface only and define the following density of states: \mathcal{D}_s^\pm spin (up,down) s-band density and \mathcal{D}_d^\pm spin (up,down) d-band density (up = majority, down = minority). Assume $\mathcal{D}_d^+ = 0$ and $\mathcal{D}_s^\pm = \mathcal{D}_s \equiv F$, all of these densities being taken at the Fermi surface. The quantity

$$P_e = \frac{\mathcal{D}^+ - \mathcal{D}^-}{\mathcal{D}^+ + \mathcal{D}^-} = - \frac{\mathcal{D}_d^-}{\mathcal{D}} \quad (12)$$

where \mathcal{D} , \mathcal{D}^\pm represent total densities of states, could be measured, say, in a photoemission experiment. The polarization of the pickup electron is given by:

$$P_p = \frac{(A_s \mathcal{D}_s^+ + A_d \mathcal{D}_d^- - A_s \mathcal{D}_s^- - A_d \mathcal{D}_d^+)}{(A_s \mathcal{D}_s^+ + A_d \mathcal{D}_d^+ + A_s \mathcal{D}_s^- + A_d \mathcal{D}_d^-)} \quad (13)$$

where A_s and A_d are the square of the pickup amplitudes for s and d electrons. Equations (12) and (13) then give;

$$P_p = \frac{-|P_e| \mathcal{D}}{(F(\eta-1) + \mathcal{D})} \quad (14)$$

where $\eta = A_s/A_d$.

The densities of states, \mathcal{D} and F , in eq. (14) were taken from the S-layer Ni(100)

calculation of Wang and Freeman.¹⁰ They found $P_e = -.55$. (The experimental value is quoted¹¹ as $-.3$ with possibly large errors.)

To calculate η we assume a positron surface ground state binding energy of 2.0 eV. Nieminen and Hodges³ had not calculated surface states for Ni so this value is based on trends in their result. The activation energy for Ni (100) has been measured⁵ to be .75 eV which gives $E_p = 1.25$ eV. Taking $e_f = 9.2$ eV¹² and $\phi_- = 5.1$ eV the maximum allowed positronium energy is $E_K = .45$ eV. The value of P_p was found to be fairly insensitive to the value taken for the surface width over the range 2-3 a.u. This value was estimated from ref.¹⁰ to be 2.0 a.u. The decay of d electron wavefunctions at the surface of Ni is, of course, too complicated to be represented by a single mass. From an exponential fit to the calculated charge density in ref.¹⁰ we estimated κ (eq. 5b). This gave $m_d \approx 5m_e$ and $m_s \approx .8m_e$. Taking $m_s = m_e$, with $m_d = 4m_e$ and $m_d = 10m_e$, we found $\eta \approx 4.0$ and 12.0 respectively. Then from Eq. (14) we have $P_p = -.33$ for $m_d = 4m_e$ and $P_p = -.18$ for $m_d = 10m_e$. One sees that large d effective mass causes the polarization of electron pickup in positron desorption to be about half that of photoemission. Note that P_e and P_p above threshold have a more complicated dependence on the density of states because one has to sum over the densities of states up to the Fermi surface. However, one still expects a similar effect of large effective d mass on minority spin pickup above threshold. We calculate η at .1 eV above threshold to be approximately 2.0 for $m_d = 4m_e$ and 2.5 for $m_d = 10m_e$. This value of positronium energy is where the observed sign reversal of the polarization of photoemitted electrons is largest.¹¹

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REFERENCES

1. A.P. MILLS, Jr., Solid State Communications 31, 623 (1979); I.J. ROSENBERG, A.H. WEISS, K.F. CANTER, Journal of Vacuum Science and Technology 17, 253 (1980); LYNN K.G., Physical Review Letters 43, 391 (1979); A.P. MILLS, Jr., Physical Review Letters 41, 1828 (1978).
2. J. BARDEEN, Physical Review Letters 6, 57 (1961).
3. R.M. NIEMINEN and C.H. HODGES, Physical Review B 18, 2568 (1978).
4. R.M. NIEMINEN and M. MANNINEN, Solid State Communications 15, 403 (1974).
5. I.J. ROSENBERG, A.H. WEISS, K.F. CANTER, Journal of Vacuum Science and Technology 17, 253 (1980).
6. A.P. MILLS, Jr., L. PFEIFFER, Physical Review Letters, 43, 1961 (1979).
7. S. CHU, A.P. MILLS, Jr., C.A. MURRAY, Physical Review B 23, 2060 (1981).
8. J. ROSE, private communication.
9. A. KOYMEN, D. GIDLEY, private communication.
10. C.S. WANG, A.J. FREEMAN, Physical Review B 21, 4585 (1980).
11. W. EIB, S.F. ALVARADO, Physical Review Letters 37, 444 (1976).
12. C.S. WANG, J. CALLAWAY, Physical Review B 15, 298 (1977).